

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Torsten Gottschalk-Gaudig et al.

Group Art Unit: 1792

Serial No.: 10/738,543

Examiner: Elena Tsoy Lightfoot

Filed: December 17, 2003

For: WATER-WETTABLE SILYLATED METALOXIDES

Attorney Docket No.: WAS 0611 PUS

DECLARATION OF DR. TORSTEN GOTTSCHALK-GAUDIG

Mail Stop Amendment
Commissioner for Patents
U.S. Patent & Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Dr. Torsten Gottschalk-Gaudig, do hereby declare and state as follows:,

1. I studied organic chemistry and coordination chemistry from 1987 to 1994 at the Universität Erlangen-Nürnberg, and from 1994 to 1997 pursued my doctoral studies, under the supervision of Prof. D. Sellmann, Institut für Anorganische Chemie II, at the same university. I achieved my Ph.D *summa cum laude*, my thesis titled “Activation and Stabilization of Small Molecules by Ruthenium Complexes Bearing Tetradentate Thioether-Thiolate Ligands. I pursued post doctoral studies under Prof. K.G. Caulton at Indiana University during 1998 to 1999, and then under Prof. Sellmann at the Universität Erlangen-Nürnberg during 1999-2000. In November of 2000 I accepted the position of Research and Development Manager, SILICA, at Wacker Chemie AG, and since June of 2003 I have been Platform Manager, SILICA, for that company. I am the author or co-author of some 26 scientific publications, and am a named inventor for numerous patent families filed worldwide. A list of publications and patent families is attached.

2. I am a coinventor of the subject matter disclosed and claimed in U.S. Patent Application Serial No. 10/738,543, and am familiar with the subject matter of the

application, the Office Actions received from the United States Patent and Trademark Office, and the references cited by the Patent Examiner.

3. The *Barthel* reference, U.S. 5,686,054 discloses a method of producing silica with exceptionally high hydrophobicity and zero detectable surface silanol content. *Barthel* requires the silica to have a methanol number ≥ 50 .

4. Very hydrophobic silicas are important in the processing of silica-filled hydrophobic polymers, as they are easily incorporated into the polymer, for example in a single or twin screw mixer, Banbury mixer, kneading cascade, or the like. In contrast, hydrophilic silicas are difficult to incorporate, and at high filler levels can produce dry-appearing crumb which is difficult or impossible to further process. Therefore, the aim of Dr. Barthel was to increase the hydrophobicity to as high a level as possible. This was accomplished by a specific process where the silica is loaded with silylating agent in the form of a mist at relatively low temperature, followed by reaction at a much higher temperature.

5. Dr. Barthel recognized that the amounts of silylating agent could vary over a relatively wide range, a range which is dependent upon such factors as type of silylating agent, type of silica, surface area of silica, and specific processing method. Some silylating agents can also react with previously bonded silyl groups rather than silanol groups. However, while the ranges are necessarily broad, they are only broad so as to enable one skilled in the art to produce a "*Barthel*" silica, i.e. one with a very high methanol number, one which is highly hydrophobic and has no detectable silanol groups. *Barthel* would not motivate one skilled in the art to produce only a partly hydrophobicized silica. *Barthel* teaches only fully hydrophobicized silica.

6. *Tojo* has also been cited by the Examiner. One skilled in the art, reading *Tojo*, understands that *Tojo* wishes all the silanol groups of untreated silica to be "blocked" by silyl groups bearing functional groups which can bond to the diene rubber of *Tojo*. *Tojo* does not disclose any silica having a low methanol number or low surface silanol content. *Tojo* contrasts his specific silyl functional groups with other silyl groups such as trimethylsilyl groups, because the latter do not provide sufficient aging resistance. Thus, *Tojo* requires the silyl "functional" groups to be alkenyl, chloroalkenyl, or chloroalkyl groups.

7. The Examiner appears to believe that if the carbon content of the claimed silica is within the carbon content range of *Barthel* or *Tojo*, that the remaining claimed properties, e.g. surface coverage, wetting angle, surface silanol group content, and methanol content will also be met. This is incorrect, as is well known to the skilled artisan, and is borne out even by the Examples of *Barthel*. *Barthel's* Example 1 and Example 2 (comparative) silicas were both prepared from the same type of silica, with the same specific surface area, the same silylating agent, and the same amount of silylating agent. Yet, the Comparative Example had half the carbon content of the *Barthel*-processed silica, and a lower methanol number, although still very high.

8. To further illustrate that there is no direct relationship between carbon content, silanol content, and methanol number, a series of Examples and Comparative Examples were prepared under my direction, in the laboratories of Wacker Chemie A.G. in Burghausen, Germany. These examples are set forth in the Table on the next page, and employ various silylating agents, in various amounts, with silicas of different surface areas. In the Table, the silylating agents used are identified as follows:

DMDCS	dimethyldichlorosilane
HMDS	hexamethyldisilazane
OH-PDMS	hydroxyl-terminated-polydimethylsiloxane
MTCS	methyltrichlorosilane
TMES	trimethylethoxysilane.

Both HMDS and TMES result in formation of $(\text{CH}_3)_3\text{Si-O}$ groups on the silica surface, and in this respect these silylating agents are similar.

The details of the additional examples/comparative examples are as follows. The details for Examples 1-5 may be found in the specification.

Example 6 (according to the invention)

At a temperature of 25°C and under N₂ inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m²/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N20 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 2.56 g of a mixture of 0.56 g of H₂O and 2.0 of MeOH and 4.29g of dimethyldichlorosilane. The silica thus loaded is reacted at 250°C in a 100 L drying cabinet under N₂ for a residence time of 2 h. The analytical data are listed in the Table.

Comparative Example C1 (non-inventive; aim:
same carbon content as Example 1 but different silica)

At a temperature of 25°C and under N₂ inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m²/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N10 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 2.56 g of a mixture of 0.56 g of H₂O and 2.0 g of MeOH and 4.29 g of dimethyldichlorsilane. The silica thus loaded is reacted at 250°C in a 100 L drying cabinet under N₂ for a residence time of 2 h. The analytical data are listed in the Table.

Example 3 (non-inventive; aim:
same carbon content as Example 1 but different organosilicon compound)

At a temperature of 25°C and under N₂ inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m²/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N20 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 8.21 g of a mixture of 1.79 g of H₂O and 6.42 g of MeOH and 9.90 g of methyltrichlorosilane. The silica thus loaded is reacted at 250°C in a 100 L drying cabinet. The analytical data are listed in the Table.

Example 7 (2.1 parts of silylating agent)

At a temperature of 25°C and under N₂ inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HC1 content of less than 100 ppm, and with a specific surface area of 200 m²/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N20 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.35 g of H₂O and 2.10 g (*i.e.* 2.1 parts with respect to silica; 0.09 mmol/g per 100 m²/g silica of trimethylsiloxy groups) of trimethylethoxysilane. The silica thus loaded is reacted at 200°C in a 100 l drying cabinet under N₂ for a residence time of 2 h. The analytical data are listed in Table 1.

Comparative Example C3 (2.1 parts of silylating agent)

At a temperature of 25°C and under N₂ inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HC1 content of less than 100 ppm, and with a specific surface area of 100 m²/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N20 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.47 g of H₂O and 2.10 g (*i.e.*, 2.1 parts with respect to silica; 0.18 mmol/g per 100 m²/g silica of trimethylsiloxy groups) of hexamethyldisilazane. The silica thus loaded is reacted at 80°C in a 100 l drying cabinet under N₂ for a residence time of 2 h and then cleaned from by-products at 150°C for 1 h. The analytical data are listed in the Table.

Comparative Example C4 (2.1 parts of silylating agent and lower BET surface area)

At a temperature of 25°C and under N₂ inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HC1 content of less than 100 ppm, and with a specific surface area of 100 m²/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® C10 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.35 g of H₂O and 2.10 g (*i.e.*, 2 parts with respect to silica; 0.09 mmol/g per 100 m²/g silica of trimethylsiloxy groups) of

trimethylethoxysilane. The silica thus loaded is reacted at 200°C in a 100 l drying cabinet under N₂ for a residence time of 2 h. The analytical data are listed in Table 1.

Table 1

Example	Silica Surface Area (m ² /g)	Silylating Agent, wt.%	Carbon Content wt.%	% SiOH	Water Wettable ?	Methanol Number
1	200	2.86 DMDCS	0.56	80	yes	0
2	300	2.67 HMDS	0.95	82	yes	5
3	150	1.33 HMDS	0.41	74	yes	15
4	200	1.00 OH-PDMS	0.35	94	yes	0
5	200	2.00 OH-PDMS	0.61	84	yes	0
6	200	2.56 DMDCS	0.82	71	yes	0
C1	100	2.56 DMDCS	0.85	43	no	45
C2	200	9.90 MTCS	0.81	48	no	40
7	200	2.10 TMES	0.54	72	yes	0
C3	100	2.10 HMDS	1.13	55	no	43
C4	100	2.10 TMES	0.58	44	no	52
Barthel 1	200	32 DMDCS	3.0	Not Detectable	no	55
Barthel 2 (Comparative)	200	32 DMDCS	1.5	Detectable	no	40
Subj. Inv.	25 - 500	0.015 - 0.15 mmol/g	> 0 to 2.0	Surface Silanol 0.9 - 1.7 SiOH/nm ²	yes	≥ 30
Barthel	25 - 400+	2 - 100 wt.%	> 1 to 2+	0 (col. I, II, 44-49)	no	> 50

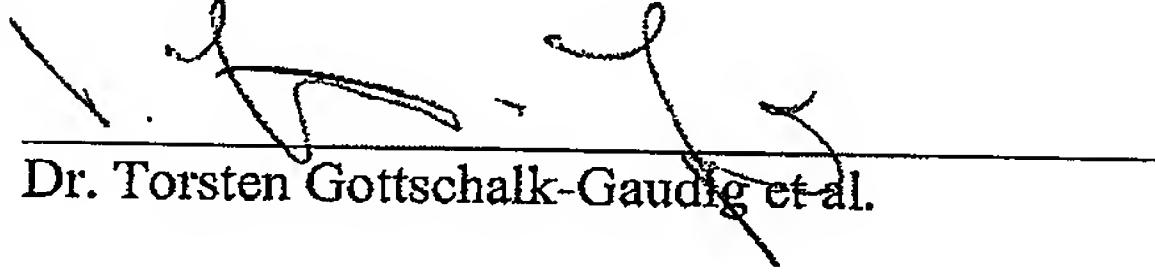
9. One can see from these results that there is no relationship between carbon content, and for example, methanol number. The values of many parameters are specified in the claim. Six of these, for example, are

- (1) contact angle $\theta < 180^\circ$;
- (2) degree of coverage $1\% < \tau < 50\%$;
- (3) density of surface silanol groups ≥ 0.9 and ≤ 1.7 SiOH/nm²;
- (4) carbon content > 0 and less than 2 wt. %;
- (5) methanol number < 30 ;
- (6) amount of silylating agent 0.015 to 0.15 mmol/g per 100 m²/g silica surface area.

Each of these must be simultaneously met; not just one, and meeting only one limitation does not infer that any or all of the others are necessarily met. For example, Comparative Examples C1, C2, C3, and C4 all meet the carbon content limitation, with carbon contents ranging from 0.58 to 1.13 weight percent, yet none of these silicas meet Applicants' claim requirement of a methanol number < 30 . Asserting that if one limitation is met, all others are met, is somewhat like stating that someone has won the lottery when only one of his six numbers matched the drawn numbers.

10. Not only do neither *Barthel* or *Tojo* disclose any silica falling within Applicants' claims, most importantly, both direct the skilled artisan away from the claimed silica. One skilled in the art, reading *Tojo* and *Barthel*, would be motivated to select the silylating conditions so as to produce only silicas with a very high methanol number. Both these references direct the skilled artisan in a direction opposed to what Applicants have done.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.



Dr. Torsten Gottschalk-Gaudig et al.

Dated: 06/02/2003

List of publications:**Scientific Publications:**

1. Ridaoui, H.; Donnet, J.-B.; Balard, H.; Kellou, H.; Hamdi, B.; Barthel, H.; Gottschalk-Gaudig, T.; Legrand, A.-P. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* (2008), 330(1), 80-85
2. Donnet, J.-B.; Balard, H.; Nedjari, N.; Hamdi, B.; Barthel, H.; Gottschalk-Gaudig, T. *Journal of Colloid and Interface Science* (2008), 328(1), 15-19
3. Kaetzel, U.; Gottschalk-Gaudig, T.; Stintz, M.; Barthel, H. *Chemie Ingenieur Technik* (2008), 80(9), 1408
4. Kellou, H.; Hamdi, B.; Brendle, E.; Gottschalk-Gaudig, T.; Barthel, H.; Ridaoui, H.; Balard, H.; Donnet, J.-B. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* (2008), 327(1-3), 90-94
5. Donnet, J.-B.; Ridaoui, H.; Balard, H.; Barthel, H.; Gottschalk-Gaudig, T. *Journal of Colloid and Interface Science* (2008), 325(1), 101-106
6. Kaetzel, U.; Vorbau, M.; Stintz, M.; Gottschalk-Gaudig, T.; Barthel, H. *Particle & Particle Systems Characterization* (2008), 25(1), 19-30
7. Kaetzel, U.; Bedrich, R.; Stintz, M.; Ketzmerick, R.; Gottschalk-Gaudig, T.; Barthel, H. *Particle & Particle Systems Characterization* (2008), 25(1), 9-18
8. Gottschalk-Gaudig, T.; Barthel, H. *Organosilicon Chemistry VI: From Molecules to Materials* (2005), Volume 2, 902-909.
9. Zhuang, Y.; Sampurno, Y. A.; Sudargho, F.; Steward, G.; Barthel, H.; Mayer, E.-P.; Gottschalk-Gaudig, T.; Stintz, M.; Kaetzel, U.; Nogowski, A.; Goldstein, M.; Philipossian, A. *Materials Research Society Symposium Proceedings* (2007), 991(Advances Challenges in Chemical Mechanical Planarization), 233-238
10. Horozov, T. S.; Binks, B. P.; Gottschalk-Gaudig, T. *Physical Chemistry Chemical Physics* (2007), 9(48), 6398-6404
11. Katzel, U.; Richter, T.; Stintz, M.; Barthel, H.; Gottschalk-Gaudig, T. *Physical Review E: Statistical, Nonlinear, and Soft Matter Physics* (2007), 76(3-1)
12. Dreyer, M.; Gottschalk-Gaudig, T.; Barthel, H. *European Coatings Journal* (2007), (7-8), 39-44
13. Barthel, H.; Gottschalk-Gaudig, T.; Dreyer, M. *Surfactant Science Series* (2007), 137(Powders and Fibers), 565-609
14. Dreyer, M.; Gottschalk-Gaudig, T.; Barthel, H. *Farbe + Lack* (2007), 113(4), 28-129
15. Kaetzel, U.; Stintz, M.; Babick, F.; Barthel, H.; Gottschalk-Gaudig, T. *AIChE Spring National Meeting, Conference Proceedings*, Orlando, FL, United States, Apr. 23-27, 2006 (2006)
16. Barthel, H.; Dreyer, M.; Gottschalk-Gaudig, T.; Litvinov, V.; Nikitina, E. *Organosilicon Chemis-*

- try V: From Molecules to Materials (2003), 752-766.
- 17. Barthel, H.; Dreyer, M.; Gottschalk-Gaudig, T.; Litvinov, V.; Nikitina, E. Macromolecular Symposia (2002), 187, 573-584
 - 18. Sellmann, D.; Gottschalk-Gaudig, T.; Häussinger, D.; Heinemann, F. W.; Hess, B. A. Chemistry-A European Journal (2001), 7(10), 2099-2103
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 - 21. Sellmann, D.; Heinemann, F.; Gottschalk-Gaudig, T. Zeitschrift fuer Naturforschung, B: Chemical Sciences (1999), 54(9), 1122-1124
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 - 22. Gottschalk-Gaudig, T.; Huffman, J. C.; Caulton, K. G.; Gerard, H.; Eisenstein, O. Journal of the American Chemical Society (1999), 121(13), 3242-3243
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 - 24. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. Inorganic Chemistry (1998), 37(16), 3982-3988
 - 25. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. Inorganica Chimica Acta (1998), 269(1), 63-72
 - 26. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W.; Knoch F. Chemische Berichte/ Recueil (1997), 130(5), 571-579

Patents:

- 1. EP1433749 Process for the production of wettable, gentle hydrophobic and finely dispersed silica comprising a silylated surface
- 2. EP1473296 Silica treated with alpha-silanes and process for its manufacturing
- 3. DE10349082 Water based dispersions and/or emulsions of RTV-1 silicone sealants stabilized by (partial) silylated pyrogenic silica which do not cleave off VOC or contain tensides
- 4. DE10360464 Dispersions of silica comprising at least two different types of silica particles having different isoelectrical points
- 5. WO05092989 Emulsions of W/O- / O/W-typ comprising an oil phase, a water phase and sintered aggregates of pyrogenic silica at their interphase

6. WO06018144 Particles comprising a core consisting of metal oxides, metal/silicon oxides, silicon dioxide and/or silicone resins having protected isocyanate groups on the surface
7. WO06018112 pyrogenic silica stabilized emulsion comprising low amounts of electrolytes showing enhanced flowing porpties
8. WO06081979 Hydroxy alkyl functional particles as filler obtainable by conversion of metal oxide, organo polysiloxane resins and/or colloidal particles with cyclic organo siloxanes in the presence of water or alcohol
9. WO06058657 Cationic silica for dispersions for the synthesis of coatings for ink jet media
10. WO06097240 Dispersions of partially hydrophobized silica for water based resins and adhesives
11. WO07012547 Sterical stabilized silica dispersed in organic or aqueous matrix comprising high filler amounts for the use in scratch resistant coatings and nano-composite adhesives
12. WO06084629 Composition for coatings comprising particles having protected isocyanato groups at the surface
13. WO08000302 Process for the production of pyrogenic silica using a combustion chamber comprising a cooling to produce silica with low amounts of impurity atoms and low amounts coarse-grained particles
14. WO07048691 Zwitterionic particles modified with ammonium-alkyl-sulfonated siloxanes and their use as filler in composite materials for the production of membranes
15. EP1845136 Alkylsilane-modified pyrogenic silica as rheological additive basic media like amine hardeners for epoxy
16. WO07113095 Core-shell particles with a substructure inducing selfcleaning properties